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SECTION – 1

INTRODUCTORY REVIEW

Polymer science is an interdisciplinary and unique branch of chemistry comprising of chemical, physical, engineering, processing and theoretical aspects. The Polymeric compounds are most important products of modern chemical industries. Concentration focus is now on the synthesis and development of entirely new aliphatic-aromatic polymers which are high performance polymers, with outstanding thermal stability and solubility, flame resistance, degradability provide great impetus to the discovery of a variety of thermo stable and processable polymers.

There is an amazing variety in the properties of polymeric materials which play a critical and ubiquitous role in everyday life [1].

Nowadays, we need polymer which can be used repeatedly and within the maximum range of temperature and should be environment friendly. It should be easily processable and relevant in their various uses [2, 3].

Polymer science is of increasing importance for everyone's daily life. They find wide use in almost all consumer products and for special purposes such as plastic parts, clothes, lightweight jackets, shoes, sports articles, electronic items, medical accessories, bottles, containers, fishing lines, gaskets, ropes, lenses and optical coatings and photo resistors for semiconductor manufacture[4, 5]. Digital printing technologies use a variety of polymers as critical components. They also find wide use in packaging materials, films and film supports, fibers, textiles, industrial yarns, automobile bumpers, lubricants, coating agents, adhesives, fibers and other disposable articles, as well as in biomedical applications, implants and controlled drug delivery devices [6, 7].

Polymer science has enormous impact on contemporary materials science. Its aim is to grant the basis for the formation and characterization of polymeric materials and an understanding of structure and property relationships.

The synthesis and development of entirely new aliphatic-aromatic polymers with outstanding thermal stability and solubility, flame resistance, degradability provide great impetus to the discovery of a variety of thermostable and processable polymers. There is a significant category of high performance and engineering materials, which exhibit good thermal stability, solvent resistance and good mechanical properties [8].

High-performance polymer syntheses have been attempted by researchers for outstanding properties like improved fluorescent brightening effect, colouristic fastness properties [9]. Therefore research and development of polymers to improve stability, fluorescent brightening as well as overall fluorescent brightening effect and also colouristic fastness properties are now of major interest.

The thermal stability of polymers can be increased either by increasing crystallinity, cross linking and / or by removing thermo oxidative weak links [10]. Research indicates that the use of the aromatic ring in the main chain of polymer increases the thermal property of polymers [11, 12]. A variety of polymers containing s-triazine nuclei in the main chain have been reported [13-16].

The synthesis and characterization of a wide variety of s-triazine based novel comb-like polymers which contain three long alkyl side chains in each repeating unit have been described by Jui-Kun Lin et al. [17].

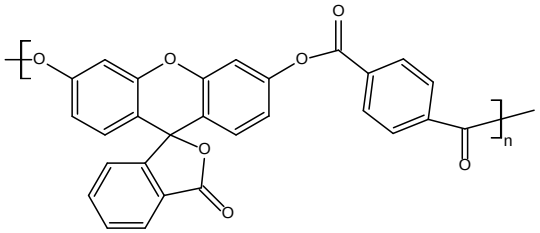
The synthesis and properties of s-triazine ring containing polymers in the main chain, such as, polyesters and polyamides is important as it is known that polyamides containing s-triazine as a heterocyclic unit in the main chain exhibit excellent thermal stability with improved solubility, fluorescence and coloristic fastness [18].

Coumarin compounds and its derivatives play an important role in organic chemistry. Coumarin and its derivatives are useful in a number of fields, such as perfumes, cosmetics and pharmaceutical industrial production. Special applications are reported in the field of optical brightening agents, dispersed fluorescent and laser dyes.

Such work has been done by Chengmei Liu et al. [19] with coumarin as a monomer in polymers and these polymers were stable up to 280^{o}C. Researchers have studied the photophysics of coumarin compounds due in part to the tenability of their absorbance and fluorescence [20-23].

Photoluminescent sensors have been demonstrated to be valuable tools for the environmental control of many compounds, including polycyclic aromatic hydrocarbons and pesticides, based on the measurement of their native luminescence [24-27]. Unfortunately, many of those organic compounds display similar luminescence properties, explanation the required of selectivity typically found in such methods.

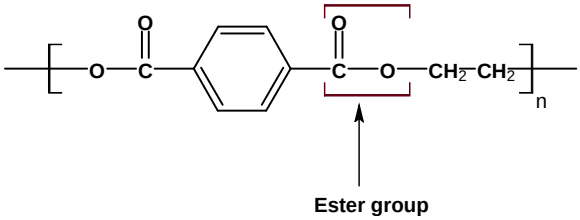
Various types of light emitting polymers by using fluorescent dye as a building block for potential application as luminescence conversion materials have been synthesized and characterized by P. Uthirakumar et al. [28].



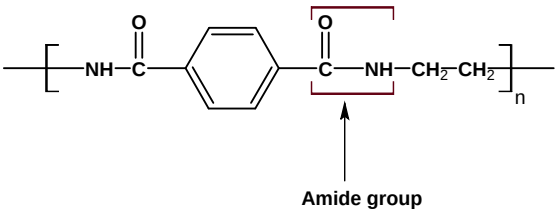
Coumarin and its derivatives confirm enough fluorescence in the visible light range to be used in laser dyes and organic light-emitting diodes (LEDs) [29, 30].

Many synthetic coumarin have a wide spectrum of biological activity and also show fluorescence [31]. This makes it possible to use them as fluorescent probes, markers, laser media and optical brighteners [32-34].

Polyesters are an important class of high performance and engineering polymers, which find use in a number of diverse applications. Different kind of polyesters has been synthesized over the past decades from various types of diacid chlorides and diols.



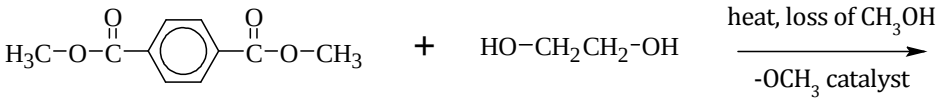
Polycondensation of difunctional monomers involve the esterification of diacids and diols, diacid chlorides and diols, or the ester transaction reaction of diesters and diols [35, 36]. The polyesters containing pendant bulky groups and flexible segments with high thermal stability and enhanced solubility in organic solvents have been reported [37, 38].



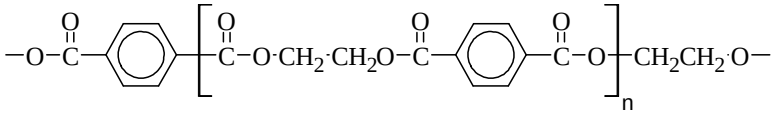
Polyamides are defined as polymers, which contain recurring (-CONH-) amide groups in the polymer chain. They are known as nylons, originally a trade name, which later became the generic name given to linear aliphatic polyamides. Polymeric amides are found in many polypeptides (proteins) that constitute a variety of animal organisms and in silk and wool. It was a search to prepare substitutes for the latter that led to the commercial development of synthetic polyamides known as nylons.

Aromatic polyamides are used as safety and resistant materials i.e. currently diverse cut-resistant and bullet-resistant materials, as well as personnel, structure and vehicle applications can be used due to the high tensile strength and modulus of these polyamides [39], membranes [40], biomaterials and polyamide systems for medical applications as screws, hooks, plates, pins, cages, rods, knee and hip replacements.

Structural design materials like automobile, aircraft and building devices such as fuel tubing, joints, tires, vehicle tubes etc. for vehicle tubes i.e. tubing used in vacuum brake systems, as fuel barriers, as connectors for fuel lines, as joints for fuel tanks, or the like are due to common features of the semi aromatic resins as their moldability and recyclability beside with high levels of residence stability, heat resistance, chemical resistance, excellent adhesive properties, compatibility with other resins, small fuel permeation, excellent stiffness and fuel barrier properties [41-44], packaging materials, filters, gas barrier films and coatings; fibers, resins and films with diverse properties and applications [45-49].



Dimethyl Terephthalate + Ethylene Glycol



Poly(Ethylene Terephthalate)

Even though having the usual characteristics, there are certain drawbacks associated with aromatic polyamides because of their infusible and insoluble nature in organic solvents, which restrict their processing.

An aromatic polymers containing 1, 3, 4- oxadiazole rings in the main chain express high thermal resistance in oxidative atmosphere, good hydrolytic stability, low dielectric permittivity, high toughness and other special properties which are determined by the electronic structure of this particular heterocycle [50-53]. The incorporation of oxadiazole and imide rings together with flexible groups in the polymer chain is anticipated to make available a combination of high-performance properties and processability, principally in thin films and coatings.

It is well known that polyamides containing heterocyclic units in the main chain possess excellent thermal stabilities. The present work has been carried out with the aim to

synthesize and characterize high performance polymers. The polymers are based on hetero cyclic moieties like s-triazine and substituted coumarin and also aromatic compounds like amines and diols with expectation to be fluorescent, highly stable and to fulfill all the criteria of recent high performance polymers by high temperature polycondensation method.

SECTION – 2

EXPERIMENTAL WORK

This section describes synthesis and characterization of aromatic polyesters, copolyesters, polyamides and coployamides as shown below:

Part-I Compasses of four schemes as under:

Scheme 1: Ten polyesters from 6-(Oxadiazolyl)-2, 4-bis-(7-hydroxy-coumarin-3-carbonylchloride)-1, 3, 5-triazine [ODCCT] and various diols.

Scheme 2: Ten copolyesters from 6-(Oxadiazolyl)-2, 4-bis-(7-hydroxy-coumarin-3-carbonylchloride)-1, 3, 5-triazine [ODCCT] and various diols.

Scheme 3: Five polyamides from 6-(Oxadiazolyl)-2, 4-bis-(7-hydroxy-coumarin-3-carbonylchloride)-1, 3, 5-triazine [ODCCT] and various diamines.

Scheme 4: Five copolyamides from 6-(Oxadiazolyl)-2, 4-bis-(7-hydroxy-coumarin-3-carbonylchloride)-1, 3, 5-triazine [ODCCT] and various diamines.

Part-II Compasses of four schemes as under:

Scheme 5: Ten polyesters from 6-(7-Hydroxy 3-Methyl Coumarin)-2, 4-bis-(7-Hydroxy-Coumarin-3-carbonyl Chloride)-1, 3, 5-triazine [MCCCT] and various diols.

Scheme 6: Ten copolyesters from 6-(7-Hydroxy 3-Methyl Coumarin)-2, 4-bis-(7-Hydroxy-Coumarin-3-carbonyl Chloride)-1, 3, 5-triazine [MCCCT] and various diols.

Scheme 7: Five polyamides from 6-(7-Hydroxy 3-Methyl Coumarin)-2, 4-bis-(7-Hydroxy-Coumarin-3-carbonyl Chloride)-1, 3, 5-triazine [MCCCT] and various diamines.

Scheme 8: Five polyamides from 6-(7-Hydroxy 3-Methyl Coumarin)-2, 4-bis-(7-Hydroxy-Coumarin-3-carbonyl Chloride)-1, 3, 5-triazine [MCCCT] and various diamines.

Part-III Compasses of four schemes as under:

Scheme 9: Ten polyesters from 6-(Oxadiazolyl)-2, 4-bis-(7-Hydroxy-Coumarin-3-carbonyl Chloride)-1, 3, 5-triazine [ODCCT] and various diols.

Scheme 10: Ten copolyesters from 6-(Oxadiazolyl)-2, 4-bis-(7-Hydroxy-Coumarin-3-carbonyl Chloride)-1, 3, 5-triazine [ODCCT] and various diols.

Scheme 11: Five polyamides from 6-(Oxadiazolyl)-2, 4-bis-(7-Hydroxy-Coumarin-3-carbonyl Chloride)-1, 3, 5-triazine [ODCCT] and various diamines.

Scheme 12: Five copolyamides from 6-(Oxadiazolyl)-2, 4-bis-(7-Hydroxy-Coumarin-3-carbonyl Chloride)-1, 3, 5-triazine [ODCCT] and various diamines.

Part-IV Compasses of four schemes as under:

Scheme 13: Ten polyesters from 6-(Oxadiazolyl)-2, 4-bis-(7-Hydroxy-Coumarin-3-carbonyl Chloride)-1, 3, 5-triazine [ODCCT] and various diols.

Scheme 14: Ten copolyesters from 6-(Oxadiazolyl)-2, 4-bis-(7-Hydroxy-Coumarin-3-carbonyl Chloride)-1, 3, 5-triazine [ODCCT] and various diols.

Scheme 15: Five polyamides from 6-(Oxadiazolyl)-2, 4-bis-(7-Hydroxy-Coumarin-3-carbonyl Chloride)-1, 3, 5-triazine [ODCCT] and various diamines.

Scheme 16: Five copolyamides from 6-(Oxadiazolyl)-2, 4-bis-(7-Hydroxy-Coumarin-3-carbonyl Chloride)-1, 3, 5-triazine [ODCCT] and various diamines.

Part-V Compasses of four schemes as under:

Scheme 17: Ten polyesters from 6-(Carbazolyl)-2, 4-bis-(7-Hydroxy-Coumarin-3-carbonyl Chloride)-1, 3, 5-triazine [CACCT] and various diols.

Scheme 18: Ten copolyesters from 6-(Carbazolyl)-2, 4-bis-(7-Hydroxy-Coumarin-3-carbonyl Chloride)-1, 3, 5-triazine [CACCT] and various diols.

Scheme 19: Five polyamides from 6-(Carbazolyl)-2, 4-bis-(7-Hydroxy-Coumarin-3-carbonyl Chloride)-1, 3, 5-triazine [CACCT] and various diamines.

Scheme 20: Five copolyamides from 6-(Carbazolyl)-2, 4-bis-(7-Hydroxy-Coumarin-3-carbonyl Chloride)-1, 3, 5-triazine [CACCT] and various diamines.

SECTION – 3

CHARACTERISATION

The polyesters, copolyesters, polyamides and copolyamides have been synthesized and characterized by their IR spectra, NMR spectra, solubility, solution viscosity measurements, thermo gravimetric analysis (TGA) and differential scanning calorimetric (DSC) spectra.

Solubility of polymers was checked by dissolving polymers in polar, non polar, halogenated and non halogenated solvents.

Infrared spectra of polymers have been measured using KBr pellets on the IR instrument of Perkin Elmer FT-IR Spectrometer and the study of nuclear magnetic resonance spectroscopy of some of the polymers.

Solution viscosity measurements have been carried out for the polyesters using Ubbelohde viscometer. Intrinsic viscosity is obtained from the combined plot of reduced viscosity versus concentration and inherent viscosity versus concentration, according to Krammer and Huggin's equations.

Thermo gravimetric analysis of the representative polymers have been carried out on the thermo balance operated at heating rate and have been analyzed according to the graphical methods proposed by Broido and Horowitz.

The melting point, the glass transition temperature and crystallization temperature of representative polymers have been determined by deferential scanning calorimeter.

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